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(54) Title: PRODUCTION OF LIGHT OLEFINS FROM ALIPHATIC HETERO COMPOUNDS (57) Abstract The process for the production of light olefins from a feedstock comprising at least an aliphatic hetero compound comprising contacting said feedstock with a silicoaluminophosphate molecular sieve at effective process conditions to produce light olefins.		

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PRODUCTION OF LIGHT OLEFINS
FROM ALIPHATIC HETERO COMPOUNDS

REFERENCE TO RELATED APPLICATION

This application is a continuation-in-part of copending U.S. Serial Number 426,213, filed October 4, 1982.

FIELD OF THE INVENTION

The present invention relates to a new catalytic process for the production of light olefins, i.e., olefins having not more than four carbon atoms, from a feedstock comprising aliphatic hetero compounds or mixtures thereof in the presence of a silicoaluminophosphate molecular sieve catalyst.

BACKGROUND OF THE INVENTION

As a result of the limited availability and high cost of petroleum sources the cost of producing chemicals from such petroleum sources has been steadily increasing. Further, many in the chemical industry, as well as elsewhere, have raised the dire prediction of significant oil shortages in the not too distant future. As a result, the search for an alternative, low cost and more readily available raw material for chemical synthesis has been intense with the ultimate goal being the derivation of valuable chemical products from non-petroleum sources.

Such readily available sources are methanol, ethanol and their derivatives which may be manufactured from non-petroleum sources such as by fermentation or from synthesis gas, i.e. a mixture

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of oxides of carbon and hydrogen. Synthesis gas may be derived by the combustion of any carbonaceous material including coal, or any organic material, such as hydrocarbons, carbohydrates and the like. Thus, the use of methanol and its derivatives to form chemical products is particularly desirable in providing such a non-petroleum based route. The manufacture of methanol from synthesis gas by a heterogeneous catalytic reaction is presently an efficient commercial process.

Although methanol and its derivatives have for some time been considered as desirable starting materials for the manufacture of chemicals (which it is, e.g., in the manufacture of formaldehyde), the use of such as a replacement for petroleum or natural gas in commercial chemical syntheses has not been vast. If processes can be developed for the use of methanol and its derivatives for the commercial manufacture in large volume of chemical products or intermediates then the present dependence on petroleum sources as the basic raw material for chemical synthesis may be substantially lessened.

One proposed way to use methanol and its derivatives to manufacture chemical products is by catalytically converting them with crystalline aluminosilicate zeolites. Representative of the various contemplated processes using such crystalline aluminosilicate zeolites, and as more completely discussed hereinafter, are those processes disclosed in U.S. Patent Nos.: 3,894,107; 4,046,825; 4,062,905; 4,079,095; 4,079,096;

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3,911,041; and 4,049,573. What appears to be evident from the above patents, as well as other patents, is that the process is tied to the particular catalyst employed yielding differences in: product ratios (as well as by-product formation); catalyst life; conversion to product; selectivity to product; catalyst attrition; and the effects from additives to the catalytic process. The significance of these differences is readily apparent by reviewing the divergent results of the published art wherein various catalysts have been employed for the conversion of methanol to light olefin products. Representative of this art are: European Application No. 6,501 (catalyst is HZSM-5); European Application No. 2,492 (catalyst is Mn exchanged 13X zeolite); German Offen. 2,909,928 (catalyst is Fe exchanged Silicalite); Angew. Chem. Int. Ed., 19, 2 (1980), 126-7 (catalyst is Mn exchanged Chabazite and erionite); South African 78/2527 (catalyst is CaH-Fu-1 zeolite); and European Application 11,900 (catalyst is boron modified silica).

For example, German Offen. 2,909,928 discloses a 95-100 percent conversion with 5.2 weight percent of the product as ethylene, whereas the publication Agnew. Chem. Int. Ed., 19, 2 (1980), 126-7 discloses a conversion of about 82 percent with 35.7 weight percent of the product as ethylene.

A brief discussion of selected patents and publications will further serve to point out differences involved in the conversion of methanol and derivatives thereof to light olefin products.

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U.S. Patent No. 4,062,905 discloses a process for the conversion of methanol, dimethyl ether or mixtures thereof to hydrocarbon products rich in ethylene and propylene using a catalyst comprising a crystalline aluminosilicate zeolite characterized by pores, the major dimension of which, are less than 6 Angstroms, the pores being further characterized by pore windows of about a size as would be provided by 8-membered rings of oxygen atoms. The process is alleged to have the capability under certain conditions of producing less than 20 weight percent methane by weight of the hydrocarbon product. The claimed correlation in the patent between pore size, process conditions and the level of methane production is admittedly specifically limited to the crystalline aluminosilicate zeolites, see the quote below.

The passage beginning at column 3, line 5 (also see Example 17) of U.S. 4,062,905 demonstrates this view:

"In addition to having the hereinabove described pore size characteristics, the crystalline aluminosilicate zeolite utilized as catalyst in the present process should have the capability of producing a hydrocarbon product containing less than 20 percent and preferably not more than 10 percent by weight of methane. Thus, the calcium form of zeolite A, having pores of approximately 5 Angstroms and commonly referred to as zeolite 5A, while satisfying the pore size requirements for zeolites useful as catalysts in the process described herein, is nevertheless, not a particularly feasible catalyst since under the conversion conditions utilized in such process, this zeolite produces considerable amounts of methane, i.e. far in excess of

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the specified maximum of 20 weight percent characterizing the crystalline aluminosilicate zeolites which have been found to be effective in selectively converting methanol and/or dimethyl ether to ethylene and propylene."

Even when a crystalline aluminosilicate zeolite having the desired physical and chemical properties is employed it may not be useful as a catalyst according to the patent's process. Thus, this patent discloses that the chemical composition of an aluminosilicate which has a desirable pore size may or may not be determinative as to whether it will produce methane at a given rate such that less than 20 percent by weight methane is produced.

The specificity of the catalysts in this field is demonstrated by U.S. Patent Nos. 4,079,096 and 4,079,095 which disclose processes for the conversion of methanol, dimethyl ether or mixtures thereof to hydrocarbon products, such as ethylene and propylene, by contacting them with a catalyst comprising, respectively, a crystalline aluminosilicate zeolite of the erionite-offretite family and, the particular erionite-offretite of the crystalline aluminosilicate zeolite ZSM-34. The processes are limited to the use of crystalline aluminosilicates having substantially the same diffraction pattern as the erionite-offretite family.

U.S Patent No. 3,911,041 describes the conversion of methanol or dimethyl ether by contacting them with a crystalline aluminosilicate zeolite having a silica to alumina ratio of at least about 12, a constraint index of about 1 to 12, and containing phosphorous deposited on the crystal

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structure thereof in an amount of at least about 0.78 percent by weight. The phosphorous is disclosed as not in the framework of the crystalline aluminosilicate, as can be determined from the preparation procedure beginning at column 7, line 56 of the patent. The procedure set forth in the patent details that the crystalline aluminosilicate zeolite is formed prior to the addition of the phosphorus-containing compound, after which the phosphorous-containing compound is "reacted" with the surface sites of the zeolite to provide a surface treated material. Further, X-ray diffraction analyses of the zeolite before and after treatment with a phosphorus-containing compound showed substantially identical interplanar spacings (see Column 8, lines 54 to 64) indicating that no phosphorus was present in the framework. The surface treatment of the crystalline aluminosilicates is predicated on the patentees' belief that the number and strength of the aluminosilicates acid sites is related to the activity.

U.S. Patent No. 4,049,573 describes a crystalline aluminosilicate zeolite having a silica to alumina ratio of at least 12 and a constraint index within the approximate range of 1 to 12, and having deposited thereon (as one of several possibilities) between about 0.25 and about 10 percent by weight of phosphorus oxide in combination with between about 0.25 and about 5 percent by weight of boron oxide and between about 2 and about 15 percent by weight of magnesium oxide. As was the

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case in the above-discussed U.S. Patent No. 3,911,041, the phosphorous oxide, boron oxide and magnesium oxide are not incorporated into the zeolite framework but, instead, are added to the zeolite after the framework of the aluminosilicate zeolite has been formed, i.e. are provided as a post treatment of the aluminosilicate zeolite, apparently for the same reason.

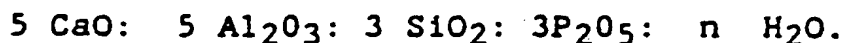
As is evident from the above, the interest in selective catalysts for the manufacture of light olefins from methanol has been achieved from a special aluminosilicate structure or by achieving modifications of aluminosilicates by deposition with special additives. As above-noted, one of these was to deposit a phosphorous-containing compound (termed "doping" herein) in combination with a number of other compounds on an aluminosilicate zeolite.

U.S. Patent Nos. 3,911,041 and 4,049,573, reports the sorption of phosphate ions onto amorphous metal oxides and combinations of metal oxides. Such sorptions of phosphate ions has been intensively studied in such areas as in the chemistry of soil, although such studies have not heretofore reported a crystalline microporous phosphate-containing material. For example, see: S.S.S. Rajan and K.W. Perrott, J. Soil Sci., 26, 257 (1975); J.A. Veith and G. Sposito, Soil. Sci., Soc. Am. J., 41, 870 (1977); E.A. Ferreiro and S.G. DeBussetto, Agrochimica, 24,184 (1980).

It has been reported (D. McConnell, Ameri. Min., 37, 609 (1952)) that certain natural aluminosilicate zeolites may have PO_2^+

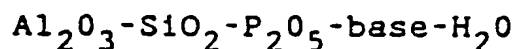
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substitution into the tetrahedral framework with such a substitution being reported in viseite which is considered to be isostructural with analcime. D. McConnell reported an elemental composition of:



This report should be viewed cautiously, if not with skepticism, in view of the considerable question of agreement on the X-ray powder diffraction patterns of such a substituted viseite and analcime owing to the highly defective structure (with dangling - OH groups wherever tetrahedral cation vacancies occur) resorted to in order to substantiate such structures as being isostructural.

R.M. Barrer and D.J. Marshall (J. Chem. Soc., 1965, 6616 and 6621) reported the attempted substitution of phosphorus in aluminosilicates during hydrothermal crystallizations in the system, in respect to the following:



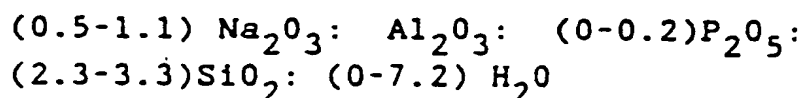
Although phosphate was observed to co-precipitate with the aluminosilicates in this system there was no evidence that an aluminosilicophosphate framework had formed.

R.M. Barrer and M. Liquornick (J. Chem. Soc., Dalton Trans., 2126 (1974)) reported that by use of metakaolinite and phosphoric acid, and in some instances by further addition of silica, that zeolites were formed having an extremely low content of phosphorous with a maximum of 0.0117 atoms of

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phosphorus present per atom of aluminium. The authors explanation for this very low phosphorous content is that phosphate anions were trapped in cavities within the zeolite framework rather than actually being in the framework.

U.S Patent No. 3,443,892 discloses a process for making Zeolite X by mixing aluminum phosphate with hot sodium silicate to give an as-synthesized product having the general formula:



No chemical data is disclosed by the patentee for determining the framework structure and the patent requires that the ratio of SiO_2 to Na_2O in the reaction mixture must be less than 1.

The synthesis of aluminosilicophosphate zeolite analogues having phosphorus incorporated into the tetrahedral sites of the zeolite-type framework during hydrothermal synthesis employing substantial amounts of alkali metal cations has been reported by E.M. Flanigen and R.W Grose at Advances in Chem., Series No. 101 pages 76-101 (1971). (Also see: Canadian Patent No. 911,410, issued October 3, 1972 to Robert W. Grose and Edith M. Flanigen) In this report the authors reported compositions with the following types of zeolite-type frameworks: analcime, chabazite, phillipsite-harmotome, Type A zeolite, Type L zeolite, and Type B (P) zeolite. These compositions were reported to contain between 5 and 25 percent by weight P_2O_5 incorporated

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into the zeolite-type frameworks. The substitution of phosphorus for silicon did not appear to impart beneficial properties to the compositions not possessed by analogous aluminosilicate compositions, although differences were reported in some of the compositions, e.g. reduced adsorption capacity and reduced thermal stability on thermal activation. Many of the physical and chemical properties of the phosphorus-substituted analogues were inferior to those of the unsubstituted species.

DISCLOSURE OF THE INVENTION

This invention comprises a process for the catalytic conversion of a feedstock comprising one or more aliphatic hetero compounds comprising alcohols, halides, mercaptans, sulfides, amines, ethers and carbonyl compounds or mixtures thereof to a hydrocarbon product containing light olefinic products, i.e., C₂, C₃ and/or C₄ olefins. The feedstock is contacted with a silicoaluminophosphate molecular sieve at effective process conditions to produce light olefins. Silicoaluminophosphate molecular sieves which produce light olefins are generally employable in the instant process. The preferred silicoaluminophosphates are those described in U.S. Patent No. 4,440,871. Silicoaluminophosphate molecular sieves employable in the instant process are more fully described hereinafter.

It has been found that silicoaluminophosphate molecular sieves are extremely efficient catalysts for the conversion of a feedstock comprising aliphatic hetero compounds, preferably

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methanol, ethanol, dimethyl ether, diethyl ether or mixtures thereof, to light olefins and that the two carbon, three carbon, and four carbon (C_2-C_4) light olefin product content of the hydrocarbon reaction products generally comprises a major portion of the hydrocarbon products while methane and aromatics typically comprise a minor portion thereof.

DESCRIPTION OF THE INVENTION

The instant process relates to making light olefins containing 2 to 4 carbon atoms wherein said process comprises contacting a feedstock with a silicoaluminophosphate molecular sieve comprising a molecular framework of $[AlO_2]$, $[PO_2]$ and $[SiO_2]$ tetrahedral units, at effective process conditions to produce such light olefin products. It should be noted that the $[AlO_2]$ tetrahedral unit has a net negative charge and the $[PO_2]$ tetrahedral unit has a net positive charge, although such are not designated herein as such.

The term "light olefins" will be used hereinafter to refer to olefins having two to four carbon atoms, inclusive. Although other hydrocarbon products are formed, the products of particular interest herein are the light olefins and they are preferably produced as the major hydrocarbon products i.e., over 50 mole percent of the hydrocarbon product is light olefins. The effect of an aromatic diluent on silicoaluminophosphate molecular sieves in the catalytic formation of light olefins is disclosed in copending U.S. Serial No. (Att. Doc. No. 13493-1), filed concurrently herewith

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and commonly assigned. Silicoaluminophosphate molecular sieves employable in the instant process will be more fully discussed hereinafter.

It is disclosed in copending U.S. Serial No. 426,213 that by use of silicoaluminophosphate molecular sieves as the catalyst(s) for the conversion of such a feedstock that, in general, higher feedstock conversions and selectivities (sometimes referred to as the "Molar Efficiency") to light olefin products may be obtained as compared to that obtained by use of the prior art aluminosilicate zeolites as catalysts.

It has also been discovered that by use of specific silicoaluminophosphate molecular sieves and anaromatic diluent that the selectivities to C_2 to C_4 olefin products (i.e., ethylene, propylene, and butenes) of at least about 25 molar percent, based on the total hydrocarbon products formed, may be obtained, preferably in excess of 50 mole percent.. Further, the selectivity for the conversion of aliphatic hetero compounds to such olefin products may be in excess of 75 mole percent when specific silicoaluminophosphate molecular sieves are employed. Further, high molar conversions i.e., preferably at least about 70 percent and most preferably at least about 90 percent, based on the moles of feestock to products, may be obtained while forming a minimum molar amount of methane (less than about ten (10) molar percent and preferably less than about five (5) molar percent) and while forming only minor amounts of saturated hydrocarbons and C_5 and higher hydrocarbons (typically less than

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about 10 molar percent). An additional bonus is that certain silicoaluminophosphate molecular sieves as employed in the instant process are believed to have increased catalyst life with respect to the conversion of the instant feedstock to light olefin products as compared with the crystalline aluminosilicates (e.g. the ZSM-type). (For example, see example 2 of U.S.P. 4,079,095)

The instant process employs a feedstock comprising "aliphatic hetero compounds". The term "aliphatic hetero compounds" is employed herein to include alcohols, halides, mercaptans, sulfides, amines, ethers and carbonyl compound (aldehydes, ketones, carboxylic acids and the like). The aliphatic moiety preferably contains from 1 to about 10 carbon atoms and more preferably contains from 1 to about 4 carbon atoms. Suitable reactants include lower straight or branched chain alkanols, their unsaturated counterparts, and the nitrogen, halogen and sulfur analogue of such. Representative of suitable aliphatic hetero compounds include: methanol; methyl mercaptan; methyl sulfide; methyl amine; dimethyl ether; ethanol; ethyl mercaptan; ethyl chloride; diethyl ether; methylethyl ether; formaldehyde; dimethyl ketone; acetic acid; n-alkyl amines; n-alkyl halides and n-alkyl sulfides having n-alkyl group having 3 to 10 carbon atoms; and mixtures thereof.

The instant process is preferably carried out in the vapor phase such that the feedstock is contacted in a vapor phase in a reaction zone with a silicoaluminophosphate molecular sieve at effective

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process conditions such as to produce light olefins, i.e., an effective temperature, pressure, WHSV (Weight Hourly Space Velocity) and, optionally, an effective amount of diluent, correlated to produce light olefins. Alternatively, the process may be carried out in a liquid phase. When the process is carried out in the liquid phase the process necessarily involves the separation of products formed in a liquid reaction media and can result in different conversions and selectivities of feedstock to product with respect to the relative ratios of the light olefin products as compared to that formed by the vapor phase process.

The temperature which may be employed in the process may vary over a wide range depending, at least in part, on the selected silicoalumino-phosphate catalyst. In general, the process can be conducted at an effective temperature between about 200°C and about 700°C, preferably between about 250°C and about 600°C., and most preferably between about 300°C and about 500°C. Temperatures outside the stated range are not excluded from the scope of this invention, although such do not fall within certain desirable embodiments of the invention. At the lower end of the temperature range and, thus, generally at the lower rate of reaction, the formation of the desired light olefin products may become markedly slow. At the upper end of the temperature range and beyond, the process may not form an optimum amount of light olefin products. Notwithstanding these factors, the reaction will still occur and the feedstock, at least in part, can

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be converted to the desired light olefin products at temperatures outside the range between about 200°C and about 700°C.

The process is effectively carried out over a wide range of pressures including autogenous pressures. At pressures between about 0.001 atmospheres and about 1000 atmospheres, the formation of light olefin products will be effected although the optimum amount of product will not necessarily form at all pressures. The preferred pressure is between about 0.01 atmospheres and about 100 atmospheres. The pressures referred to herein for the process are exclusive of the inert diluent, if any is present, and refer to the partial pressure of the feedstock as it relates aliphatic hetero compounds and/or mixtures thereof. Pressures outside the stated range are not excluded from the scope of this invention, although such do not fall within certain desirable embodiments of the invention. At the lower and upper end of the pressure range, and beyond, the selectivities, conversions and/or rates to light olefin products may not occur at the optimum although light olefin products can be formed.

The process is effected for a period of time sufficient to produce the desired light olefin products. In general, the residence time employed to produce the desired product can vary from seconds to a number of hours. It will be readily appreciated by one skilled in the art that the residence time will be determined to a significant extent by the reaction temperature, the silico-

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aluminophosphate molecular sieve selected, the WHSV, the phase (liquid or vapor) selected, and, perhaps, selected process design characteristics. -

The process is effectively carried out over a wide range of WHSV for the feedstock and is generally between about 0.01 hr^{-1} and about 100 hr^{-1} and preferably between about 0.1 hr^{-1} and about 40 hr^{-1} . Values above 100 hr^{-1} may be employed and are intended to be covered by the instant process, although such are not preferred.

The instant process is most preferably carried out under process conditions comprising a temperature between about 300°C and about 500°C , a pressure between about 0.1 atmosphere (one atmosphere equals 14.7 psia) to about 100 atmospheres, utilizing a WHSV expressed in hr^{-1} for each component of the feedstock having a value between about 0.1 and about 40. The temperature, pressure, and WHSV are each selected such that the effective process conditions, i.e., the effective temperature, pressure, and WHSV, are employed in conjunction, i.e. correlated, with the selected silicoaluminophosphate molecular sieve and selected feedstock such that light olefin products are produced.

The instant process is generally carried out in the presence of one or more inertly diluents which may be present in the feedstock in an amount between about 1 and about 99 molar percent, based on the total number of moles of all feed and diluent components fed to the reaction zone (or catalyst). Typical of diluents which may be employed in the

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instant process are helium, argon, nitrogen, carbon monoxide, carbon dioxide, hydrogen, water(steam), paraffins, hydrocarbons (such as methane and the like), aromatic compounds, mixtures thereof, and the like. The preferred diluents are believed to comprise mixtures of water (steam) and aromatic diluents. The use of aromatic diluents is disclosed in copending U.S. Serial No. (Attorney Docket No. 13,493-1) filed concurrently herewith and commonly assigned.

The instant process may be carried out in a batch, semi-continuous, or continuous fashion. The process can be conducted in a single reaction zone or a number of reaction zones arranged in series or in parallel, or it may be conducted intermittently or continuously in an elongated tubular zone or a number of such zones. When multiple reaction zones are employed, it may be advantageous to employ one or more of such silicoaluminophosphate molecular sieves in series to provide for a desired product mixture. Owing to the nature of the process, it may be desirable to carry out the instant process by use of the silicoaluminophosphates in a dynamic (e.g. fluidized or moving) bed system or any system of a variety of transport beds rather than in a fixed bed system. Such systems would readily provide for any regeneration (if required) of the silicoaluminophosphate molecular sieve catalyst after a given period of time. If regeneration is required, the silicoaluminophosphate molecular sieve catalyst can be continuously introduced as a moving bed to a regeneration zone where it can be regenerated, such

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as for example by removing carbonaceous materials by oxidation in an oxygen-containing atmosphere. In the preferred practice of the invention, the catalyst will be subject to a regeneration step by burning off carbonaceous deposits accumulated during reactions.

SILICOALUMINOPHOSPHATES

The selection of the silicoaluminophosphate molecular sieve catalysts for the instant process is preferably related, in part, to the desired product mixture sought to be obtained. The selected silicoaluminophosphate molecular sieve desirably has a kinetic pore diameter (average kinetic diameter in Angstroms, \AA) such that the selectivity to the light olefin products is greater than 50 molar percent. Accordingly, at least a portion, preferably a major portion, of the pores have an average kinetic diameter characterized such that the adsorption capacity (as measured by the standard McBain-Bakr gravimetric adsorption method using given adsorbate molecules) shows adsorption of oxygen (average kinetic diameter of about 3.46\AA) and negligible adsorption of isobutane (average kinetic diameter of about 5.0\AA). More preferably the average kinetic diameter is characterized by adsorption of Xenon (average kinetic diameter of about 4.0\AA) and negligible adsorption of isobutane and most preferably by adsorption of n-hexane (average kinetic diameter of about 4.3\AA) and negligible adsorption of isobutane. Negligible adsorption of oxygen or xenon is adsorption of less than four percent by weight of the adsorbate based

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on the weight of the silicoaluminophosphate and adsorption of oxygen or xenon is adsorption of greater than or equal to four percent by weight of the adsorbate based on the weight of the silicoaluminophosphate. Negligible adsorption of n-hexane or isobutane is adsorption of less than two percent by weight of the adsorbate based on the weight of the silicoaluminophosphate and adsorption of n-hexane or isobutane is adsorption of greater than or equal to two percent by weight of the adsorbate based on the weight of the silicoaluminophosphate. Although it is clear that factors other than just the kinetic pore size will affect the products formed, including any occlusion of the pores, the exact nature of such other factors or their exact effect on the products formed are not understood at present. It is believed that the kinetic diameter of the pores of the silicoaluminophosphate molecular sieve is related to the products formed. Although a specific silicoaluminophosphate may not have a kinetic pore diameter within the desired or preferred range the silicoaluminophosphate may be modified by depositing or impregnating such with cations, anions, salts and/or compounds that occlude or otherwise result in the modification of a silicoaluminophosphate having a large pore size to one having a kinetic pore diameter(s) within the desired or preferred range.

Techniques which may be employed to effect the diminution of the pore size of a silicoaluminophosphate molecular sieve are generally known in the art. Such procedures generally involve the

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introduction to a pore of a pore size restricting material and may involve such procedures as (1) impregnating the silicoaluminophosphate with a solution comprising a solvent or solubilizing agent for such a pore restricting material (one or more) in an amount sufficient to deposit the desired weight of such pore restricting material to the silicoaluminophosphate such that the desired pore size is obtained and/or (2) exchanging the silicoaluminophosphate with a solution containing the pore size restricting material. The impregnation or deposition of the pore restricting materials may be generally accomplished by heating the silicoaluminophosphate at an elevated temperature to evaporate any liquid present to effect deposition or impregnation of the pore restricting material into the interior and/or onto the exterior surface of the silicoaluminophosphate, or by the exchange of cations present in the silicoaluminophosphate with cations that provide for the desired kinetic pore size. Alternatively, the pore restricting material may be formed on the silicoaluminophosphate from an emulsion or slurry containing the pore restricting material by heating the silicoaluminophosphate as described above. Impregnation and exchange procedures are generally the preferred techniques because they utilize and introduce the pore restricting material more efficiently than other procedures such as coating procedures since a coating procedure is generally not able to effect substantial introduction of the pore restricting material onto the interior surfaces

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of the silicoaluminophosphate. In addition, coated materials are more generally susceptible to the loss of the pore restricting materials by abrasion.

Suitable pore restricting materials include alkali metal, alkaline earth metals, transition metals and the salts thereof including inorganic and organic salts such as: nitrates, halides, hydroxides, sulfates and carboxylates. Other pore restricting materials generally employed in the art for such are also believed to be employable herein.

In carrying out the instant process the silicoaluminophosphate molecular sieves may be admixed (blended) or provided sequential to other materials which may provide some property which is beneficial under process conditions, such as improved temperature resistance or improved catalyst life by minimization of coking or which is simply inert under process conditions. Such materials may include synthetic or naturally occurring substances as well as inorganic material such as clays, silicas, aluminas, crystalline aluminosilicate zeolites, metal oxides and mixtures thereof. In addition, the silicoaluminophosphate molecular sieves may be formed with materials such as silica, alumina, silica-alumina, silica-magnesia, silico-zirconia, silica-thoria, silica-beryllia, silica-titania, as well as ternary compositions, such as silica-alumina-thoria, silica-alumina-zirconia and clays present as binders. The relative proportions of the above materials and the silicoaluminophosphate may vary widely with silicoaluminophosphate content ranging

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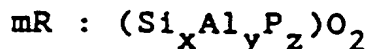
between about 1 and about 99 percent by weight of the composite.

Silicoaluminophosphate molecular sieves employable in the instant process will be referred to hereinafter, solely for point of reference herein, as "SAPO" molecular sieves, or as "SAPOs" if the reference is to the class as a whole as employed herein. This designation is simply made for the sake of convenient reference herein and is not meant to designate a particular structure for any given silicoaluminophosphate (SAPO) molecular sieve. Although, the class of SAPO's employable in the instant process is that class which will produce C_2 , C_3 and/or C_4 olefins from the feedstock at a sufficient temperature and related process conditions. The class of SAPO's described in U.S. Patent No. 4,440,871, said U.S. Patent being incorporated herein by reference thereto, is particularly well suited for use in the present process. The members of the class of SAPO's employed hereinafter in the examples will be characterized simply by referring to such members as SAPO-5, SAPO-11, etc, i.e., a particular species will be referred to as SAPO-n where "n" is a number specific to a given class member as its preparation is reported herein. This designation is an arbitrary one and is not intended to denote structure or relationship to another material(s) which may also be characterized by a numbering system.

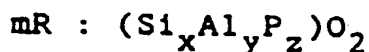
The silicoaluminophosphates of U.S Patent No. 4,440,871 are generally described as microporous

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crystalline silicoaluminophosphates the pores of which are uniform and have nominal diameters of greater than about 3 Angstroms and whose essential empirical chemical composition in the as-synthesized and anhydrous form is



wherein "R" represents at least one organic templating agent present in the intracrystalline pore system; "m" has a value of from 0.02 to 0.3; "m" represents the moles of "R" present per mole of $(Si_xAl_yP_z)O_2$; "x", "y" and "z" represent the mole fractions of silicon, aluminum and phosphorus respectively, present as tetrahedral oxides, said mole fractions being such that they are within the pentagonal compositional area defined by points A, B, C, D and E of the ternary diagram which is FIG. 1 of the drawings of U.S. Patent No. 4,440,871, incorporated herein by reference thereto. The silicoaluminophosphates of U.S. Patent No. 4,440,871 are further characterized by characteristic x-ray powder diffraction patterns as set forth in Tables I, III, V, VII, IX, XI, XIII, XV, XVII, XIX, XXI, XXIII, and XXV, said tables being incorporated herein by reference thereto. U.S. Patent No. 4,440,871 further characterizes the silicoaluminophosphate materials as having three-dimensional microporous framework structure of PO_2^+ , AlO_2^- and SiO_2 tetrahedral units, and whose essential empirical chemical composition on an anhydrous basis is:



where in R represents at least one organic templating agent present in the intracrystalline

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pore system; "m" represents the moles of "R" present per mole of $(Si_xAl_yP_z)O_2$ and has a value of from zero to 0.3; "x", "y" and "z" represent respectively, the mole fractions of silicon, aluminum and phosphorus present in the oxide moiety, said mole fractions being within the compositional area bounded by points A, B, C, D and E on the ternary diagram which is FIG. 1, said silicoaluminophosphate having a characteristic x-ray powder diffraction pattern which contains at least the d-spacings set forth below in any one of Tables I, III, V, VII, IX, XI, XIII, XV, XVII, XIX, XXI, XXIII or XXV. The calcined forms of the above described silicoaluminophosphates are also disclosed in U.S. Patent No. 4,440,871.

EXPERIMENTAL PROCEDURE (LIGHT OLEFIN PRODUCTION)

The production of light olefins in the examples was carried out by mixing about 0.5 gram of a selected SAPO with 2.5 grams of quartz chips (20-30 U.S. Standard mesh). The resulting mixture was then placed in a 1/4 inch (outside diameter) No. 304 stainless steel tubular reactor having a wall thickness of 0.035 inch. The tubular reactor was immersed in a fluidized heated sand bath having electrical resistance heaters provided for maintaining the sand bath and the tubular reactor at the desired temperature. Thermocouples were provided for measurement of the reactor temperature.

A selected feedstock was introduced to the tubular reactor by means of a Model 100 Altex Metering Pump (from Altex Corporation, a subsidiary of the Beckmann Corporation) concurrently with a

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stream of diluent with toluene, nitrogen and water (steam) being employed as diluents (unless otherwise noted in the examples hereinafter). The pressure employed in the examples was the autogenous pressure (about one (1) to about two (2) atmospheres unless otherwise noted. The ratios of these components are reported as weight ratios. When nitrogen was employed as a diluent it was introduced at a flow rate of about 5 cubic centimeters per minute.

The effluent from the tubular reactor (the reaction products) was analyzed. The liquid component of the effluent was collected at room temperature and subsequently analyzed by vapor phase chromatography, whereas the gaseous component of the effluent was sampled and analyzed directly from the effluent stream by vapor phase chromatography.

The analyses of both the liquid and vapor components of the effluent from the tubular reactor were carried out by programmed temperature chromatography having a thermal conductivity or flame detector with a programmed increase in the chromatographic column's temperature over the chromatographic analysis. The analysis of the liquid and vaporous components of the effluent, including the analysis of all standards was carried out using chromatographic techniques by use of the following chromatographic instruments:

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	Phase Analyzed	
	<u>Liquid</u>	<u>Vapor</u>
Chromatograph	Varian 3700	Hewlett-Packard
Column	20 feet x 1/8 inch (O.D.) stainless steel	11 feet x 1/8 inch (O.D.) stainless steel
Packing	10% Carbowax Chrom T 60/80 mesh	Porapak R

Unless otherwise noted, the Molar Conversion to a particular product is given as a percentage. When a product was not detected (ND) or if only a trace amount was qualitatively detected such is reported as ND or Trace, respectively. The silicaluminophosphates employed in the following examples are denominated according to the nomenclature of U.S. Patent No. 4,440,871 as SAPO-34. The SAPOs were calcined prior to their use in the examples. The following examples are provided to exemplify the invention and are not meant to be limiting in any way.

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PRODUCTION OF LIGHT OLEFINS: EXAMPLESExample 1

SAPO-17 was employed in the instant-process for the conversion of a feedstock comprising water and methanol to hydrocarbon products such including light olefin products. The conversion was carried out under four different sets of process conditions at the autogeneous pressure, all of which resulted in the formation of over 50 molar percent of hydrocarbon phase as light olefin products. The formation of dimethyl ether was not detected under these process conditions and an ethylene to propylene molar ratio of about 0.8 or greater was observed in each case. The results are set forth in Table I-A.

Table I-A

	375°C ^{1, 3}			425°C ^{2, 3}		
Ethylene	30.6	37.3	36.5	47.4	53.3	52.5
Ethane	0.3	0.5	0.5	0.4	0.8	0.5
Propylene	37.4	34.8	29.3	29.5	26.0	26.4
Propane	0.2	Trace	Trace	Trace	ND	ND
Butenes	15.2	13.9	12.2	8.8	9.2	7.7
C ₅ 's	8.0	6.8	4.9	4.2	3.1	2.5
C ₆ 's	3.7	2.9	2.0	1.2	0.8	0.6
Methane	4.2	3.6	2.9	4.4	4.1	4.2
Carbon Dioxide	0.4	0.3	0.2	4.1	2.9	2.9
Hours on Stream	1	2.5	4.7	2.5	5.5	8.5

1WHSV (Methanol) = 0.86
WHSV (H₂O) = 2.00

2WHSV (Methanol) = 0.87
WHSV (H₂O) = 2.04

3The feed was a mixture of water and methanol having a weight ratio of 70/30.

Table I-A (Continued)

	450°C ^{3,4}		500°C ^{3,5}	
Ethylene	49.2	53.5	53.3	38.6
Ethane	0.4	0.5	0.4	0.3
Propylene	24.8	22.8	23.3	15.3
Propane	Trace	ND	ND	ND
Butenes	7.0	6.3	6.5	3.3
C ₅ 's	2.5	1.9	2.2	1.2
C ₆ 's	Trace	0.6	0.7	ND
Methane	6.3	6.5	6.7	15.2
Carbon Dioxide	9.8	8.0	6.9	26.8
Hours on Stream	2.5	5.6	8.6	2.5

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⁴ WHSV (Methanol) = 0.86 hr⁻¹

WHSV (H₂O) = 2.01 hr⁻¹

⁵ WHSV (Methanol) = 0.85 hr⁻¹

WHSV (H₂O) = 1.99 hr⁻¹

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Example 2

SAPO-34 was employed for the conversion of methanol to light olefin products at a temperature of 375°C, atmospheric pressure (i.e., about 15 psia), and at a WHSV (methanol) of 1.17 hr⁻¹ and a WHSV (H₂O) of 2.73 hr⁻¹. The results are set forth in Table II-A.

Table II-A

Ethylene	35.1	34.9	35.0
Ethane	Trace	0.3	0.6
Propylene	41.9	43.4	43.0
Propane	0.5	0.2	0.4
Butenes	16.8	16.5	15.8
Butane	Trace	Trace	Trace
C ₅ 's	3.3	3.3	3.6
C ₆ 's	0.7	Trace	Trace
Methane	1.2	1.2	1.5
Carbon Dioxide	0.7	0.2	0.2
Hours on Stream	1.8	3.3	6.3

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Example 3

SAPO-16 was employed according to the Experimental Procedure for the conversion of methanol to light olefin products at temperatures of 375°C and 425°C. The results are set forth in Table III-A.

TABLE III-A¹

	<u>375°</u>	<u>425°C</u>
Ethylene	0.5	3.0
Ethane	trace	0.3
Propylene	0.6	2.3
Propane	trace	trace
Butanes	trace	trace
C ₅ 's	ND	ND
Dimethyl Ether	98.9	94.7
WHSV (Methanol), hr ⁻¹	0.87	0.82
WHSV (Water), hr ⁻¹	2.03	1.91
Conversion	53	51
Hours on Stream	2	1

¹ Methane and carbon dioxide are not included in the calculation of molar efficiency.

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Example 4

SAPO-34 was employed in the instant process for conversion of a feedstock comprising methanol to light olefin products at 375°C and atmospheric pressure using a methanol to water feedstock having a weight ratio of water to methanol of 70 to 30 (WHSV (Methanol) = 0.84 hr^{-1} and WHSV (Water) = 1.96 hr^{-1}). The results are set forth in Table IV-A.

Table IV-A

Ethylene	33.7	41.3
Ethane	0.8	0.8
Propylene	42.0	42.8
Propane	0.8	0.6
Butane	Trace	ND
Butenes	18.2	11.2
C ₅ 's	1.9	1.3
C ₆ 's	Trace	ND
Methane	2.2	1.3
Carbon Dioxide	0.6	0.7
Hours on Stream	1.1	3.3

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Example 5

SAPO-35 was employed to produce a hydrocarbon mixture containing ethylene and propylene according to the above described Experimental Procedure. The results at a process temperature of 350°C and 370°C and at the autogenous pressure are set forth in Table V-A.

Table V-A¹

	<u>350°C</u>	<u>375°C</u>
Ethylene	43.9	42.8
Ethane	ND	0.4
Propylene	23.7	31.2
Propane	0.5	1.3
Butenes	4.1 ²	8.0
Butane	ND	Trace
C ₅ 's	2.1	2.9
C ₆ 's	Trace	1.4
Methane	12.9	11.5
Carbon Dioxide	4.5	0.6
Dimethyl Ether	8.5	ND
Conversion	64	100
Hours on stream	0.25	1

¹ WHSV (at 350°C): Methanol = 1.11 hr⁻¹
Water = 2.60 hr.⁻¹

WHSV (at 375°C): Methanol = 2.60 hr⁻¹
Water = 2.43 hr.⁻¹

² Approximate value due to methanol interference on the gas chromatographic analysis.

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Example 6

SAPO-44 was employed to convert a feedstock, comprising methanol and water according to the above described Experimental Procedure. The temperature was 375°C the pressure was the autogenous pressure and the process was carried out for a period of 1 hour. The WHSV for methanol and water were respectively 0.85 and 1.99 with the methanol conversion being 45 molar percent. The results are set forth in Table VI-A.

Table VI-A

Ethylene	17.7
Ethane	6.3
Propylene	13.3
Propane	9.5
C ₄ 's ¹	7.5
C ₅ 's	1.1
C ₆ 's	ND
Methane	5.5
Carbon Dioxide	2.8
Dimethyl Ether	36.1

¹ Approximate value due to methanol interference on the gas chromatograph

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Example 7

SAPO-34 was employed in the instant process to convert a molar mixture of water and methanol to light olefin products according to the above discussed Experimental Procedure. Three runs were carried out at varying molar amounts of methanol and both with and without the use of a diluent and with varying amounts of water present. The temperature was 375°C and the pressure was the autogeneous pressure. The results demonstrate the increase in selectivity to light olefin products (at constant conversion) obtained when diluent is employed in the instant process. The results of the three runs are set forth in Tables VII-A, VIII-A, and IX-A.

Table VII-A^{1,2}

Ethylene	39.9	41.5
Ethane	1.0	0.8
Propylene	42.1	41.6
Propane	0.7	Trace
Butenes	12.3	12.0
C ₅ 's	2.2	1.8
C ₆ 's	Trace	Trace
Methane	1.4	1.3
Carbon Dioxide	0.3	0.3
Hours on Stream	4	5.5

¹ The weight ratio of water to methanol was 70:30. Nitrogen was used as an inert diluent.

² WHSV (MeOH): 0.91 hr⁻¹
WHSV (H₂O) : 2.12 hr⁻¹

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Table VIII-A^{1,2}

Ethylene	27.8	36.8
Ethane	1.2	1.2
Propylene	44.4	48.1
Propane	0.7	0.7
Butenes	19.2	10.2
C ₅ 's	4.2	1.5
C ₆ 's	0.6	Trace
Methane	1.9	1.4
Carbon dioxide	0.2	0.2
Hours on Stream	1	4.0

¹ Weight ratio of water to methanol was 30 to 70 with nitrogen employed as an inert diluent.

² WHSV (MeOH): 0.84
WHSV (H₂O) : 0.36

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Table IX-A^{1,2}

Ethylene	28.4	37.5
Ethane	1.4	2.6
Propylene	44.6	42.9
Propane	Trace	Trace
Butenes	16.9 ³	11.3
C ₅ 's	3.5	1.6
C ₆ 's	0.9	0.4
Methane	3.0	2.7
Carbon Dioxide	1.4	1.1
Hours on Stream	1	4.0

¹ Molar ratio of water to methanol was 70:30. No diluent was employed.

² WHSV (MeOH): 0.89 hr⁻¹
WHSV (H₂O) : 2.05 hr⁻¹

³ Trace amount of butane observed

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Example 8

SAPO-34 was employed as the catalyst in the instant process for the conversion of methanol to light olefins at four different temperatures. The conversion of methanol to light olefins was carried out under the autogenous pressure at temperatures of 350°C, 375°C, 400°C and 425°C. The results at these temperatures are set forth in Table X-A.

Table X-A

	<u>350°C</u>	<u>375°C</u>	<u>400°C</u>	<u>425°C</u>
Ethylene	37.0	42.6	46.0	48.6
Ethane	0.4	0.8	0.6	0.6
Propylene	39.8	41.4	36.2	30.7
Propane	0.3	0.5	0.5	0.5
Butenes	16.6	10.7	11.7	8.8
Butane	Trace	ND	ND	ND
C ₅ 's	3.8	1.7	1.6	1.3
C ₆ 's	Trace	Trace	Trace	Trace
Methane	1.7	1.3	2.0	4.1
Carbon Dioxide	0.5	0.9	1.5	5.5
Hours on Stream	0.9	5.2	6.3	6.2
WHSV (Methanol) hr ⁻¹	0.85	0.83	0.87	0.83
WHSV (Water) hr ⁻¹	1.99	1.93	2.04	1.95

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Example 9

SAPO-34 was employed in the instant process in the comparison of the conversion of two different feedstocks to light olefin products. The two feedstocks were: methanol; and dimethyl ether and water. This example was carried out under the autogenous pressure and at a temperature of 375°C. The results are set forth in Table XI-A.

Table XI-A

	Methanol ¹	Dimethyl Ether ² + Water
Ethylene	36.9	35.9
Ethane	0.8	0.4
Propylene	38.8	39.4
Propane	0.6	0.3
Butenes	11.9	17.8
Butane	Trace	Trace
C ₅	1.9	4.5
C ₆	Trace	Trace
Methane	5.5	1.4
Carbon Dioxide	3.5	0.3
Dimethyl Ether	ND	ND
Hours on Stream	1.8	0.3

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1 WHSV, hr⁻¹: 1.1 hr⁻¹ (Methanol)

2 WHSV, hr⁻¹: 1.04 hr⁻¹ (Dimethyl Ether)
3.13 hr⁻¹ (Water)

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Example 10

SAPO-34 was employed in the instant process for the conversion of methanol to light olefin products at a temperature of 375°C and at the autogenous pressure. The flow rate (WHSV) was employed at two rates to determine the effect of flow rate on light olefin production with the second flow rate being two and one half (2.5 X Flow) times that employed as the first flow rate (1X Flow). The results are set forth in Table XII-A.

Table XII-A¹

	1X Flow			2.5X Flow		
	38.2	39.4	42.6	37.3	38.6	28.7
Ethylene	0.5	0.5	0.8	0.3	0.5	0.3
Ethane	40.2	40.5	41.4	40.7	41.9	31.0
Propylene	0.4	0.4	0.5	0.2	ND	ND
Propane	14.5	13.3	10.7	15.1	13.8	10.0
Butenes	Trace	ND	ND	Trace	Trace	Trace
Butane	2.2	2.7	1.7	3.5	2.8	1.3
C ₅ 's	0.7	0.6	Trace	0.8	0.6	Trace
C ₆ 's	1.4	1.4	1.3	1.5	1.2	0.9
Methane	2.1	1.3	0.9	0.6	0.4	0.2
Carbon Dioxide	ND	ND	ND	ND	ND	27.5
Dimethyl Ether	0.9	1.7	5.2	0.8	1.5	3.8
Hours on Stream						

¹ WHSV, hr⁻¹ (1 x Flow):

(Methanol): 0.83

(Water) : 1.93

WHSV hr⁻¹ (2.5 x Flow):

(Methanol): 1.91

(Water) : 4.46

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Example 11

SAPO-34 was employed in the instant process for the conversion of ethanol to light olefins at a temperature of 400°C under the autogenous pressure and at a WHSV (ethanol) of 1.04 hr⁻¹. The results are set forth in Table XIII-A.

Table XIII-A

Ethylene	15.1	61.0	76.5
Ethane	7.6	3.3	2.2
Propylene	21.2	28.6	15.6.
Propane	31.1	Trace	ND
Butenes	16.5	4.5	1.9
C ₅	3.2	0.6	0.4
C ₆	0.8	0.3	0.3
Methane	2.3	0.9	0.5
Carbon Dioxide	2.1	0.8	0.7
Acetaldehyde	ND	ND	1.8
Hours on Stream	1.0	3.3	4.0

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Example 12

SAPO-34 was employed in the instant process for the conversion of ethanol in the presence of water to light olefin products at a temperature of 400° under the autogeneous pressure. The WHSV (Ethanol) was 0.87 hr^{-1} and the WHSV (Water) was 4.90 hr^{-1} . The results are set forth in Table XIV-A.

Table XIV-A

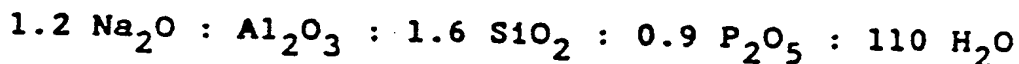
Ethylene	89.2	90.3	91.2
Ethane	1.1	1.1	1.2
Propylene	5.5	4.4	3.7
Propane	ND	ND	ND
Butenes	1.4	1.2	1.0
C ₅ 's	0.6	0.4	0.3
C ₆ 's	ND	ND	ND
Methane	0.1	0.1	0.1
Carbon Dioxide	0.5	0.4	0.3
Acetaldehyde	1.5	2.2	2.2
Hours on Stream	2.5	5.5	8.5

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EXAMPLE 13

A phosphate substituted zeolite was prepared according to the following procedure as derived from example 4 of Canadian Patent No. 911,417, issued October 3, 1972.

The substituted zeolite was prepared by mixing 24.0 grams of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, 10.4 grams of H_3PO_4 (85 wt %) and about 200 milliliters of distilled water. The resulting mixture was titrated with a concentrated solution of sodium hydroxide until the mixture had a PH of about 7.5. A precipitate was formed. This precipitate was collected by filtration and washed with about 150 milliliters of distilled water. The wet precipitate was blended with 16.0 grams of Ludox colloidal silica sol, 4.8 grams of sodium hydroxide and then dissolved in 100 milliliters of distilled water. This reaction mixture was then placed in an autoclave with an inert plastic liner and crystallized at about 150°C at the autogenous pressure for a period of about 118 hours. The reaction mixture had the following composition, expressed in oxide-molar ratios:

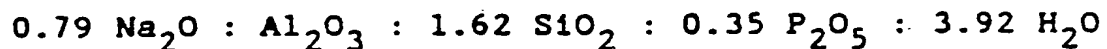


The resulting product was recovered by filtration, washed with distilled water and air dried at 110°C. The air dried product was ion-exchanged with potassium, analyzed by X-ray and the following X-ray powder diffraction pattern observed:

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<u>d</u>	<u>100 x I/Io</u>
9.46	100
6.97	21
5.61	17
5.10	21
4.72	10
4.53	5
4.36	74
4.15	7
4.02	9
3.90	43
3.62	28
3.48	16
3.14	10
2.95	95
2.92	53
2.71	9
2.64	19
2.54	14
2.33	9
2.11	7
2.08	3

The as-synthesized product was analyzed and found to contain: 13.6 wt. % P_2O_5 ; 13.3 wt. % Na_2O ; 27.7 wt. % Al_2O_3 ; 26.5 wt. % SiO_2 ; and 19.2 wt. % H_2O ; This corresponds to a composition in oxide molar ratios of:



The as-synthesized product was tested for adsorption capacities using a standard McBain-Bakr gravimetric adsorption apparatus. The following data were obtained on a sample activated at about 350°C in vacuum.

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	<u>Kinetic Diameter, Å</u>	<u>Pressure, Torr</u>	<u>Temp., °C</u>	<u>Wt. % Adsorbed</u>
O ₂	3.46	760	-183	1.6
N ₂	3.64	760	-196	-
CO ₂	3.3	760	25	-
N-butane	4.3	760	25	0.2
H ₂ O	2.65	20	25	20.9

A portion (2.0 grams) of the as-synthesized product was then refluxed for 1 hr. with 20 grams of 10 wt. percent NH₄Cl, filtered and dried for a short period at 100°C.

This composition was then employed according to the Experimental Procedure for the conversion of a feedstock containing methanol and water (WHSV (MeOH)) = 0.89 hr⁻¹ and WHSV (H₂O) = 1.08 hr⁻¹). The temperature employed was 375°C, the pressure was the autogenous pressure. The time for the conversion was 1.8 hours. The molar efficiency (given as a percentage) is given in the following Table. The molar conversion of methanol to products was only 18.4 percent. The Molar Efficiency to ethylene based on total methanol converted to hydrocarbon products was 0.7 molar percent. The results are reported in Table XV-A.

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Table XV-A

Ethylene	1.3	-
Ethane	-	
Propylene	2.5	
Propane	-	
C ₄ 's	-	
C ₅ 's	-	
C ₆ 's	-	
Methane	0.6	
Carbon Dioxide	2.1	
Dimethyl Ether	93.5	

EXAMPLE 14

SAPO-34 was employed in the instant process for the conversion of methyl chloride, n-propanol, n-butanol and certain oxygenates. The results of these experiments are set forth in Table XVI-A, Table XVII-A and Table XVIII-A. The temperatures and WHSV are set forth in the tables.

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Table XVI-A

	<u>Molar Selectivity, %</u>
Ethylene	26.0
Ethane	0.5
Propylene	50.8
Propane	5.1
C ₄ 's	12.8
C ₅ 's	5.0
C ₆ 's	Trace
Run Time (hours)	4
Methyl Chloride Conversion, Wt. %	- 20%
Temperature	350°C
Methyl Chloride Feed	5 cc/min. with 20 cc/min nitrogen

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Table XVII-A

	<u>Molar Selectivity, %</u>	
	<u>n-Propanol</u>	<u>n-Butanol</u>
Ethylene	31.4	4.3
Ethane	1.8	1.3
Propylene	50.9	11.0
Propane	-	Trace
Butenes	2.3	70.2
C ₅	2.6	Trace
C ₆	1.3	Trace
Methane	1.1	0.7
Carbon Dioxide	3.8	2.4
Propionaldehyde	4.8	Butyraldehyde 10.2
Run Time (hours)	4.0	4.0
WHSV (Hr ⁻²)	1.01	0.45
Conversion, Wt. %	100	100

Table XVII-A1, 2, 3

Feed ¹	12.5%		25%		25% Methyl		25%		25%	
	Trioxane In Water	Aqueous Formaldehyde	Trioxane In Toluene	Formate In Toluene	Acetaldehyde In Water	Propionaldehyde In Water	Run Time (hours)	Temperature (°C)	Conversion of Oxygenated Compound (Wt. %)	WHSV (Total Feed) ⁴
Ethylene	59.2	55.0	35.2	45.4	54.7	48.9	1.0	425	100	1.2
Ethane	0.8	0.9	0.3	0.9	0.9	1.2	4.9	1.0	100	1.1
Propylene	30.1	33.4	17.4	26.5	38.0	36.2	1.0	425	100	1.2
Propane	0.0	0.0	13.2	4.1	3.3	3.9	4.9	1.0	100	1.1
C ₄ Hydrocarbons	6.8	5.6	25.1	12.7	2.6	7.5	4.9	1.0	100	1.1
C ₅ Hydrocarbons	Trace	Trace	5.5	1.3	Trace	1.9	4.9	1.0	100	1.1
C ₆ Hydrocarbons	0	0	Trace	Trace	0	Trace	4.9	1.0	100	1.1
Methane	3.1	4.9	3.3	9.0	0.5	0.5	4.9	1.0	100	1.1
Run Time (hours)	1.0	1.0	1.0	1.5	4.0	1.0	1.0	425	100	1.1
Temperature (°C)	425	425	275	425	425	425	425	425	100	1.1
Conversion of Oxygenated Compound (Wt. %)	100	100	100	100	100	100	100	100	100	1.1
WHSV (Total Feed) ⁴	1.2	1.1	1.3	1.1	1.1	1.4	1.2	1.1	1.1	1.1

1 CO₂ is not included in the calculations

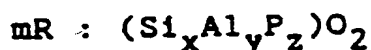
2 Feed composition expressed in Wt. %

3 All reactions were run at atmospheric pressure with N₂ as carrier gas blowing at 10-12 cc/min.4 Hr⁻²

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CLAIMSWHAT IS CLAIMED IS:

1. The process of making light olefins containing 2 to 4 carbon atoms which comprises contacting a feedstock comprising aliphatic hetero compounds and mixtures thereof with a silicoaluminophosphate molecular sieve comprising a molecular framework of $[AlO_2]$, $[PO_2]$ and $[SiO_2]$ tetrahedral units, at effective process conditions to produce light olefins presence of an aromatic diluent wherein the silicoaluminophosphate molecular sieve comprises a microporous crystalline silicoaluminophosphate whose unit empirical formula in the as-synthesized and anhydrous form is



wherein "R" represents at least one organic templating agent present in the intracrystalline pore system; "m" has a value of from zero to 0.3; "m" represents the moles of "R" present per mole of $(Si_xAl_yP_z)O_2$; "x", "y" and "z" represent the mole fractions of silicon, aluminum and phosphorus respectively, present as tetrahedral units, said mole fractions being such that they are within the pentagonal compositional area defined by points A,B,C,D and E of the ternary diagram which is FIG. 1 of the drawings of U.S. Patent No. 4,440,871.

2. The process of claim 1 wherein the silicoaluminophosphate has mole fractions of silicon, aluminum and phosphorus within the pentagonal compositional area defined by points a,

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b, c, d and e of the ternary diagram which is FIG. 2 of the drawings of U.S. Patent No. 4,440,871.

3. The process of claim 1 wherein the silicoaluminophosphate is characterized by adsorption of oxygen and negligible adsorption of isobutane.

4. The process of claim 1 wherein the silicoaluminophosphate is characterized by adsorption of Xenon and negligible adsorption of isobutane.

5. The process of claim 1 wherein the silicoaluminophosphate is characterized by adsorption of n-hexane and negligible adsorption of isobutane.

6. The process of claim 1 wherein "m" has a value of from 0.02 to 0.3.

7. The process of claim 2 wherein "m" has a value of from 0.02 to 0.3.

8. The process of claims 1 or 6 wherein the silicoaluminophosphate has the characteristic X-ray powder diffraction pattern which contains at least the d-spacings set forth in Table I.

9. The process of claims 1 or 6 wherein the silicoaluminophosphate has the characteristic X-ray powder diffraction pattern which contains at least the d-spacings set forth in Table III.

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10. The process of claims 1 or 6 wherein the silicoaluminophosphate has the characteristic X-ray powder diffraction pattern which contains at least the d-spacings set forth in Table V.

11. The process of claims 1 or 6 wherein the silicoaluminophosphate has the characteristic X-ray powder diffraction pattern which contains at least the d-spacings set forth in Table VII.

12. The process of claims 1 or 6 wherein the silicoaluminophosphate has the characteristic X-ray powder diffraction pattern which contains at least the d-spacings set forth in Table IX.

13. The process of claims 1 or 6 wherein the silicoaluminophosphate has the characteristic X-ray powder diffraction pattern which contains at least the d-spacings set forth in Table XI.

14. The process of claims 1 or 6 wherein the silicoaluminophosphate has the characteristic X-ray powder diffraction pattern which contains at least the d-spacings set forth in Table XIII.

15. The process of claims 1 or 6 wherein the silicoaluminophosphate has the characteristic X-ray powder diffraction pattern which contains at least the d-spacings set forth in Table XV.

16. The process of claims 1 or 6 wherein the silicoaluminophosphate has the characteristic X-ray powder diffraction pattern which contains at least the d-spacings set forth in Table XVII.

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17. The process of claims 1 or 6 wherein the silicoaluminophosphate has the characteristic X-ray powder diffraction pattern which contains at least the d-spacings set forth in Table XIX.

18. The process of claims 1 or 6 wherein the silicoaluminophosphate has the characteristic X-ray powder diffraction pattern which contains at least the d-spacings set forth in Table XXI.

19. The process of claims 1 or 6 wherein the silicoaluminophosphate has the characteristic X-ray powder diffraction pattern which contains at least the d-spacings set forth in Table XXIII.

20. The process of claims 1 or 6 wherein the silicoaluminophosphate has the characteristic X-ray powder diffraction pattern which contains at least the d-spacings set forth in Table XXV.

21. The process of claims 1 or 6 wherein the aliphatic hetero compound is selected from the group consisting of alcohols, ethers, amines, mercaptans, aldehydes, ketones, halides and mixtures thereof wherein the aliphatic moiety contains from 1 to about 10 carbon atoms.

22. The process of Claim 1 or 6, wherein light olefins constitute at least about 25 molar percent of the hydrocarbon products.

23. The process of Claim 22 wherein light olefin products constitute in excess of 50 molar percent of the hydrocarbon products.

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24. The process of Claim 1 or 5 wherein the feedstock is contacted with said silicoaluminophosphate at a temperature between about 200° and about 700°C.

25. The process of Claim 24 wherein the feedstock is contacted with said silicoaluminophosphate at a temperature between about 250° and about 600°C.

26. The process of Claim 1 or 6 wherein the process is conducted at a pressure between about 0.1 atmosphere and about 1000 atmospheres.

27. The process of Claim 26 wherein the process is conducted at a pressure between about 0.1 atmosphere and about 100 atmospheres.

28. The process of Claim 1 or 6 wherein said process is carried out in the vapor phase.

29. The process of Claim 1 or 6 wherein said process is carried out in the liquid phase.

30. The process of Claim 1 or 6 wherein the WHSV is between about 0.01hr^{-1} and about 100hr^{-1} .

31. The process of Claim 30 wherein the WHSV is between about 0.1hr^{-1} and about 40hr^{-1} .

32. The process of Claim 1 or 6 wherein the feedstock is a hetero compound selected from the group consisting of amines, mercaptans, aldehydes, ketones, alkyl halides and mixtures thereof wherein

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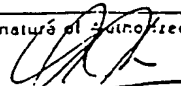
the aliphatic morety contains from 1 to about 10 carbon atoms.

33. The process of Claim 32 wherein the feedstock consists essentially of an inert diluent and at least one hetero compound.

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 86/00266

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁴		
According to International Patent Classification (IPC) or to both National Classification and IPC		
IPC ⁴ : C 07 C 11/02; C 07 C 1/20; C 07 C 1/32; C 07 C 1/253; C 07 C 1/26		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
IPC ⁴	C 07 C 1/00	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹		
Category ⁹	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X	EP, A, 0105512 (UNION CARBIDE CORPORATION) 18 April 1984, see claims (cited in the application)	1-33

<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>¹⁰ Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p> </div> </div>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
22nd May 1986	- 2 JUL. 1986	
International Searching Authority	Signature of Authorised Officer	
EUROPEAN PATENT OFFICE	 L. ROSSI	

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

V. ☒ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE

This International search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1. ☐ Claim numbers because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claim numbers because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

o) 1-33: search essentially based on examples

- 1) Claims 1-2 are not readable without an additional document
- 2) Claims 8-20 refer to tables which are not in the application or do not show d-spacings
- 3) Most of the conversions are insufficiently described, as well in the claims, as in the description

3. ☐ Claim numbers because they are dependent claims and are not drafted in accordance with the second and third sentences of PCT Rule 6.4(a).

VI. ☐ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING

This International Searching Authority found multiple inventions in this international application as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.
2. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:
3. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:
4. ☐ As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest

- ☐ The additional search fees were accompanied by applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON

INTERNATIONAL APPLICATION NO.

PCT/US 86/00266 (SA 12345)

This Annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 17/06/86

The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A- 0105512	18/04/84	AU-A- 1985183	12/04/84
		JP-A- 59084829	16/05/84
		US-A- 4499327	12/02/85